WSC – CAM – IV B

Quality Assurance and Quality Control Requirements **for the Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), MADEP-EPH-04-1.1** for the Massachusetts Contingency Plan (MCP)

Document Status: Final

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Document Chronology

Revision	Status	Date
1	Public Comment Draft	5 October 2001
2	Interim Final	12 July 2002
3	Final	10 September 2004

IV. Petroleum Hydrocarbon Methods

B. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for the Method for The Determination of Extractable Petroleum Hydrocarbons (EPH), MADEP-EPH-04-1.1, May 2004

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1.0 QA/QC REQUIREMENTS FOR THE EXTRACTABLE PETROLEUM HYDROCARBONS METHOD

1.1 Method Overview

The Extractable Petroleum Hydrocarbons (EPH) Method (the "EPH Method") is based on a solvent extraction, silica gel solid-phase extraction (SPE)/fractionation process and gas chromatography (GC) analysis using a flame ionization detector (FID) to identify and quantify both Target Polynuclear Aromatic Hydrocarbons (PAH) analytes and method-defined aliphatic and aromatic hydrocarbon fractional ranges in water, soils and sediments. Extractable aliphatic hydrocarbons are collectively quantified within two specific ranges: C_9 through C_{18}, and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantified within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150°C and 265°C. This method may also be used to identify and quantify specific Target PAH Analytes, including Diesel PAH analytes. All references to SW-846 Methods in this document refer to the United States Environmental Protection Agency's most recently published version.

The EPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection (MADEP) to evaluate human health hazards that may result from exposure to petroleum hydrocarbons entitled "Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter (MAPEP Interim Final, August, 1994) and the "Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology" (MADEP January, 2003). It is intended to produce data in a format suitable for evaluation by that approach, and that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000), including Total Petroleum Hydrocarbon (TPH).

Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuels, and certain petroleum-based lubricating oils. The EPH Method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products, that contain lower or higher boiling components or distillates of aliphatic and/or aromatic hydrocarbons that are outside the aforementioned analytical range (C_9 through C_{36} aliphatic and aromatic ranges) of the MADEP EPH Method.

1.1.1 Reporting Limits for the EPH Method

The Reporting Limit (RL) for this method for each of the collective aliphatic and aromatic ranges is approximately 20 mg/kg in soil/sediment, and approximately 100 µg/L in water. The RL for this method when used to determine Total Petroleum Hydrocarbons (TPH) is approximately 10 mg/kg in soil and approximately 100 µg/L in water. The RL of this method for the Target PAH Analytes is compound-specific, and ranges from approximately 0.2 - 1.0 mg/kg in soil/sediment, and 2 - 5 µg/L in water. These RLs reflect the sampling procedures and prescriptive analytical conditions imposed by the EPH Method. The RLs are dependent upon the concentration of the lowest analytical standard in the initial calibration and/or the percent solids of the sample

Preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for EPH samples analyzed in support of MCP decision-making are presented in Appendix IV B–1 of this document and Appendix VII-A, of WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 Requirements for the EPH Method

Each laboratory that uses the EPH Method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control samples (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of the laboratory or at the request of the data-user.

Laboratories must document and have on file an Initial Demonstration of Laboratory Capability (IDLC) for each combination of sample preparation and determinative analytical method in use. An IDLC must be completed and documented when a method is initially started up, whenever a method is substantially modified or new laboratory staff is trained to perform the EPH Method. These data must meet or exceed the performance standards as presented in Section 10.3.1 through 10.3.5 of the EPH Method and Table IV B-3 of this document. Procedural requirements for performing the IDLC can be found in SW-846 Method 8000B (Section 8.4), and Section 10.3 and Appendix 5 of the EPH Method. The data associated with the IDLC should be kept on file at the laboratory and made available to potential data-users on request.

Note: Because of the inherent difficulty in quantifying collective hydrocarbon ranges and the number of QC elements associated with the Initial Demonstration of Laboratory Capability, it should be expected that one or more of the ranges and/or optional target analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conformances. All non-conformances, along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Laboratory Capability data. This information should be kept on-file at the laboratory.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table IV B-3 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the EPH Method, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table IV B-3. It should be noted that the performance standards listed in Table IV B-3 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. A list of the required EPH Method performance standard elements and method references is presented below.

Performance Standard Element	Method Reference
Initial Calibration	CAM-IV B, Table IV B-3
Continuing Calibration	CAM-IV B, Table IV B-3
Laboratory Method Blanks	CAM-IV B, Table IV B-3
Laboratory Control Samples	The EPH Method, Section 10.4.3.3
LCS Duplicates	The EPH Method, Section 10.4.3.4
Fractionation Check Standard	The EPH Method, Section 10.4.3.7
Extraction Surrogate Recovery	CAM-IV B, Table IV B-3
Fractionation Surrogate Recovery	CAM-IV B, Table IV B-3
Potential Aromatic Breakthrough	The EPH Method, Section 10.4.2

In some cases, the standard laboratory acceptance criteria for the various QC elements may have to be modified to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatography (GC), and skilled in the interpretation of gas chromatograms for individual Target PAH Analytes and petroleum hydrocarbon ranges in environmental matrices. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results both for individual target analytes and petroleum hydrocarbon ranges with this method.

1.2 Summary of Method

This method is suitable for the analysis of waters, soils, sediments and NAPL after appropriate sample concentration and cleanup. A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using commercially available silica gel cartridges or self-packed silica gel columns. The two extracts produced (i.e., an aliphatic extract and an aromatic extract) are then re-concentrated to final volumes of 1 mL each. The extracts are then separately analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range, and is (optionally) used to identify and quantify individual concentrations of Diesel and/or other Target PAH Analytes.

Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. An average calibration factor or response factor determined using a PAH standard mixture is used to calculate a collective C_{11} through C_{22} aromatic hydrocarbon concentration. Calibration factors or response factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Diesel and Target PAH Analytes. The EPH Method marker compounds and retention time windows are summarized in Table IV B-1.

Table IV B-1 EPH Method Marker Compounds

{PRIVATE } Range/ Hydrocarbon Standard	Beginning Marker Compound	Ending Marker Compound
C_9-C_{18} Aliphatic Hydrocarbons	0.1 minutes before n-Nonane	0.1 minutes before n-Nonadecane
C_{19}-C_{36} Aliphatic Hydrocarbons	0.1 minutes before n-Nonadecane	0.1 minutes after n-Hexatriacontane
C_{11}-C_{22} Aromatic Hydrocarbons	0.1 minutes before Naphthalene	0.1 minutes after Benzo (g,h,i) Perylene

This method is based on (1) USEPA Methods 8000B, 8100, 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580A, and 3630C, SW-846, "Test Methods for Evaluating Solid Waste" (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

1.2.1 Sample Analysis Procedure

The analytical procedure for both water and solid samples are described in detail in Section 9.0 of the EPH Method. Approved matrix-specific extraction procedures are also described in Section 9.0 and are presented in Table IV B-2 below. In general, a measured volume or weight of sample, 1 L for liquids and 10 grams for solids, is extracted using the appropriate matrix-specific sample extraction technique. Samples are first extracted with methylene chloride, and then solvent-exchanged into hexane. Alternative extraction procedures other than those listed in Table IV B-2 are acceptable, provided that the laboratory can document acceptable performance. However, use of an alternative extraction procedure is considered a “significant modification” of the EPH method pursuant to Section 11.3.1.1 and as such would preclude obtaining “Presumptive Certainty” status for any analytical data produced using an alternative EPH extraction procedure.

Table IV B-2 Approved EPH Extraction Methods for Water, Soils and Sediments

SW-846 Method	Matrix	Description
3510C	Aqueous	Separatory Funnel Liquid-Liquid Extraction
3520C	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3540C	Soil/Sediment	Soxhlet Extraction
3541	Soil/Sediment	Automated Soxhlet Extraction
3545A	Soil/Sediment	Pressurized Fluid Extraction (PFE)
3546	Soil/Sediment	Microwave Extraction
3570	Soil/Sediment	Microscale Solvent Extraction (MSE)
3550C	Contaminated Solids [1]	Ultrasonic Extraction
3580A	NAPL	Solvent Dilution

1. Sonication may only be used for the extraction of highly contaminated (free product) non-soil/sediments (debris). Any other use of ultrasonic extraction is considered a "significant modification" **of the EPH Method.**

After solvent exchange with hexane, the extract is concentrated and subjected to a silica gel cleanup and fractionation step to isolate the aromatic and aliphatic components of the sample prior to GC analysis. It should be noted that the recommended hexane elution volume (20 mL) is critical and may need to be adjusted for each lot of silica gel/cartridges to optimize sample extraction and fractionation efficiencies. See Section 10.3.4 and Appendix 5 of the EPH Method for specifications on the use and evaluation of Fractionation Check Solutions.

Aliphatic and aromatic extracts are introduced into the gas chromatograph separately by directly injecting 1 to 4 µL of each extract using the solvent flush technique. Smaller volumes may be injected if automatic devices are employed.

Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with blanks and laboratory QC samples. The sequence ends when the set of sample extracts has been injected or when qualitative and/or quantitative QC criteria are exceeded.

A description of the following EPH analytical processes is presented in a flowchart format in Appendix IV B-2.

Exhibit	Description
IV B-1	EPH Aqueous Extraction
IV B-2	EPH Soil/Sediment Extraction
IV B-3	EPH Fractionation
IV B-4	EPH analysis

1.3 Method Interferences

Refer to SW-846 Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a detailed discussion of interferences associated with GC methods. Analytical interferences will vary considerably from sample to sample depending on the matrix. While general cleanup techniques are referenced or provided as part of the EPH Method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories:

- Contaminated solvents, reagents, or sample processing hardware,
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces, and
- Compounds extracted from the sample matrix to which the detector will respond.

An in-depth discussion of the causes and corrective actions for all of these interferences is beyond the scope of this guidance document. A brief discussion of the more prevalent interferences for the EPH Method is presented below.

1.3.1 Chemical Contaminants

The major contaminant source for the EPH Method is attributable to the leaching of plasticizers or other contaminants from silica gel SPE cartridges. Preferably, the silica gel cleanup and fractionation procedure described in Section 9.2 of the EPH Method should be used to minimize this source of interference.

As described in Section 11.2.6 of the EPH Method, peaks identified during the injection of Laboratory Method Blanks, and determined to be attributable to the previously described silica gel SPE cartridge interference, may adversely affect the accurate integration of the C_{11}-C_{22} aromatic hydrocarbon range area. In general, blank correction, either by the manual or automatic subtraction of contaminant peaks, **is not permissible** unless the laboratory performs a GC/MS analysis of the Laboratory Method Blank extract to confirm that the encountered contaminant(s) is not a C_{11}-C_{22} aromatic hydrocarbon range compound. The laboratory must provide a discussion in the Environmental Laboratory case narrative if this approach is used.

1.3.2 Cross-Contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of semi-volatile organic compounds. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever a sample with unusually high EPH Target PAH Analytes and/or range concentrations is encountered, it should be followed by the analysis of a method or solvent blank to check for unacceptable cross-contamination. Concentrations of any EPH target analyte or ranges which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. Laboratories should be aware that carryover from particularly refractory compounds may compromise a later sample run.

1.4 Quality Control Requirements for the EPH Method

1.4.1 General Quality Control Requirements for Determinative Chromatographic Methods

Refer to SW-846 Method 8000 for general quality control procedures for all chromatographic methods, including the EPH Method. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data.

Quality Control procedures necessary to evaluate the GC system operation may be found in the EPH Method, Sec. 9.5, and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance requirements for the analytical system may be found in Section 10 of the EPH Method.

1.4.2 Specific QA/QC Requirements and Performance Standards for the EPH Method

Specific QA/QC requirements and performance standards for the EPH Method are presented in Table IV B-3. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with "Presumptive Certainty" regarding the usability of analytical data to support MCP decisions. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for the EPH Method, parties must:

(a) Comply with the procedures described and referenced in WSC-CAM–IV B;

(b) Comply with the applicable QC analytical requirements prescribed in Table IV B-3 for this test procedure;

(c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table IV B-3 for this test method; and

(d) Adopt the reporting formats and elements specified in the CAM and Appendix 3 of the EPH Method

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

1.4.3 Additional QA/QC Requirements and Performance Standards Considerations for the EPH Method

The complete list of QA/QC requirements and performance standards described in Table IV B-3 are required only for samples analyzed for both EPH aliphatic and aromatic ranges and Target PAH Analytes. As described in Section 1.0 of the EPH Method, the analysis of Target PAH Analytes, including the diesel PAH analytes is optional. If these analytes are not reported for a particular sample, then compliance with the applicable QA/QC requirements and performance standards pertaining to these individual analytes is optional. In addition, if fractionation is eliminated and the individual EPH Method aliphatic and aromatic ranges are not quantified then only compliance with the applicable QA/QC requirements and performance standards pertaining to Total Petroleum Hydrocarbon (TPH) analysis is required.

Strict compliance with the applicable QA/QC requirements and performance standards for EPH Method "range-only" or TPH analyses, as well as satisfying the previously described reporting requirements, will still provide an LSP with "Presumptive Certainty" regarding the usability of the analytical data to support MCP decisions as described in WSC-CAM-VII A, Section 2.0 for these options.

1.4.4 Field Duplicates for EPH Analyses

As described in WSC-CAM VII A, Section 2.5, Table VII A-1, submission of Field Duplicates is recommended for drinking water samples only. However, the Field Duplicates need only be analyzed if the concentration of one or more of the EPH Target PAH Analytes or ranges in the primary sample is above the Reporting Limit (RL). Drinking water samples should be identified and specific analytical instruction for the drinking water and associated field quality control samples provided when the samples are submitted to the laboratory for analysis

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the EPH Method

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
GC Performance	Inter-laboratory consistency and comparability	(1) PAH resolution as per section 10.1.3 of the method. (2) C_9 resolution from solvent front. (3) Response ratio of C_{28} to C_{20} should be $\geq$ 0.85. (4) Surrogate and internal standards must be resolved from all aromatic and aliphatic standards. (5) Naphthalene and n-dodecane in the aliphatic fraction must be adequately resolved (see section 10.4.2 of the EPH Method)	No	Perform instrument/injection port maintenance as necessary.	Suspend all analyses until performance criteria are achieved. Report exceedances in the Environmental Laboratory case narrative.
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed (2) Calculated according to the method. (Section 9.6) (3) Retention time windows must be updated with every CCAL.	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards (2) Low standard must be $\leq$ reporting limit (RL). (3) %RSD should be $\leq$25 or "r" should be $\geq$0.99 for all compounds and ranges. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (5) If regression analysis is used, the curve must not be forced through the origin. (6) Must meet GC performance standards described in Section 10.2 of the EPH Method.	No	Recalibrate as required by method.	Sample analysis may not proceed without a valid initial calibration. Report exceedances in Environmental Laboratory case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Every 24 hours, prior to samples, and after no more than 20 samples. (2) Concentration level near midpoint of curve (3) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (4) Opening CCAL: %D or % drift must be $\leq$25 for all target PAH analytes and ranges except for n-nonane, which must be $\leq$30. (5) Closing CCAL: Up to four (4) compounds may exhibit a %D or % drift >25 but < 40. (6) Must meet GC performance standards.	No	Recalibrate as required by method. Any samples analyzed between the last CCAL that meets criteria and the one that fails criteria must be reanalyzed.	Report exceedances in the Environmental Laboratory case narrative.
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil) (3) EPH hydrocarbon ranges must be < 10% of the most stringent applicable MCP standard and Target PAH analytes must be < RL. 4) EPH hydrocarbon ranges must be $\leq$10 % of the most stringent applicable MCP cleanup standard	Yes	Locate source of contamination; correct problem; re-extract associated samples.	(1) Report non-conformances in the Environmental Laboratory case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention, should qualify the sample results. Blank contamination should also be documented in the case narrative (3) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the EPH Method

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than that used for initial calibration. (3) Concentration of LCS should be between low and mid-level standard. (4) Prepared using all the aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (5) Matrix-specific (e.g., soil, water) (6) Laboratory–determined percent recoveries (% R) must be between 40 – 140 for EPH ranges * and target PAH analytes except for n-nonane, which must be between 30 –140. (7) The individual concentrations of both Naphthalene and 2-Methylnaphthalene must be < 5% in aliphatic fraction. (See Calculation in the EPH Method, Section 10.4.2. (8) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above. * Alternatively, percent recoveries for the individual standards used for the calibration of the aliphatic or aromatic ranges may be evaluated.	Yes	(1) Recalculate %R (2) Re-extract associated samples if % R is < 40 or > 140. (3) Re-fractionate archived batch extracts if either the concentration of Naphthalene and/or 2-Methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations	(1) Report non-conformances in the Environmental Laboratory case narrative. (2) If re-extraction or re-fractionation is performed within holding time, the laboratory may report results of the re-extraction or re-fractionation only. (3) If re-extraction or re-fractionation is performed outside of holding time, the laboratory must report results of both the initial extraction/fractionation and re-extraction/re-fractionation.
Initial Calibration Verification (ICV)	Laboratory Method Accuracy	(1) Analyzed only if separate source standard is not used for LCS. (2) Percent recoveries must be between 80 – 120 for all EPH hydrocarbon ranges and target PAH analytes	No	Perform new initial calibration	(1) Sample analysis may not proceed without a valid ICV. (2) Report exceedances in Environmental Laboratory case narrative.
LCS Duplicate	Laboratory Method Precision	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all EPH aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. . (4) Recommended to be run immediately after LCS in analytical sequence. (5) Percent recoveries must be between 40 – 140 for EPH ranges and target compounds except for n-nonane, which must be between 30 – 140. (6) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 25 for target PAH analytes and EPH hydrocarbon ranges. (7) Concentration of Naphthalene and 2-Methylnaphthalene must be < 5% in aliphatic fraction	Yes	(1) Recalculate RPD and/or %R. (2) Re-fractionate archived batch extracts if either the concentration of Naphthalene and/or 2-Methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations.	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the EPH Method

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data-user). (2) Matrix-specific (e.g., soil, water) (3) Prepared by fortifying field sample with standard from source different than source used for initial calibration (4) Concentration level should be between low and mid-level standard (5) Must contain all EPH aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. . (6) Laboratory–determined percent recoveries must be between 40 – 140 for EPH ranges and target compounds except for n-nonane, which must be between 30 –140. (7) RPDs should be ≤50 for waters and soil/sediments.	Yes Only when requested by the data-user	Check LCS; if recoveries acceptable in LCS no corrective action required.	Note exceedances in Environmental Laboratory case narrative.
Matrix Duplicate	Method Precision in Sample Matrix	(1) Extracted with analytical batch (at discretion of laboratory or at request of data-user). (2) Matrix-specific (e.g., soil, water) (3) RPD should be ≤50 for PAH target analytes and EPH range data for results > 5 x RL.	Yes Only when requested by the data-user	Recheck RPD calculations.	Note exceedances in Environmental Laboratory case narrative.
Surrogates	Accuracy in Sample Matrix	(1) Minimum of 2 extraction and 1 fractionation surrogate. (2) Recommended extraction surrogates: chlorooctadecance, and ortho-terphenyl. (3) Recommended fractionation surrogate: 2-bromonaphthalene; and 2-fluorobiphenyl (optional). (4) Percent recoveries must be between 40-140 for all surrogates. (5) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above.	Yes	(1) No corrective action required if chromatogram evidences obvious interference (2) Absent obvious chromatogram interference, re-extraction or re-fractionation is required unless: Surrogates exhibit a high %R and associated EPH hydrocarbon range or target PAH analytes are not detected.	(1) Note exceedances in case narrative. (2) If re-extraction or re-fractionation yields similar surrogate non-conformances, the laboratory should report results of both extractions. (3) If re-extraction or re-fractionation is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial analysis and the re-extraction or re-fractionation. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the EPH Method

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Internal Standards * (ISs)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Recommended internal standard for EPH analysis is 5-alpha androstane. Alternatively, 1-Chloro-octadecane (COD) may also be as an internal standard for GC/MS analysis. (2) Area counts should be between 50 and 200 % of the area counts in the associated CCAL.	No	Reanalyze sample unless chromatogram evidences obvious interference (e.g. UCM).	(1) Note exceedances in case narrative. (2) If reanalysis yields similar internal standard non-conformances, the laboratory should report both results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
*Only when GC/MS is used for quantification of EPH Hydrocarbon ranges.					
Fractionation Check Standard	Laboratory Method Accuracy	(1) Performed for each new lot of silica gel cartridges. (2) Must contain all EPH aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (3) Laboratory–determined percent recoveries must be between 40 – 140 for EPH hydrocarbon ranges and target PAH analytes except for n-nonane, which must be between 30 –140. .	Yes	Re-fractionate using different volumes of hexane until recoveries are acceptable.	Note exceedances in the Environmental Laboratory case narrative.
General Reporting Issues	NA	(1) The laboratory must only report values at ≥ the sample-specific reporting limit. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) All information required in Appendix 3 of the EPH Method must be provided for each sample in a "clear and concise manner."			(1) Complete analytical documentation for diluted and undiluted analyses is to be available for review during audit. **(2) All soil/sediment samples must be reported on a dry-weight basis. See Section 9.4 of the EPH Method.** **(3) Performance of dilutions must be documented in the Environmental Laboratory case narrative.**

GC = Gas Chromatography
MS = Matrix Spike
%RSD = Percent Relative Standard Deviation
NA = Not Applicable
RL = Reporting Limit

"r" = Correlation Coefficient
RPDs = Relative Percent Differences
UCM = Unresolved Complex Mixture
PAH = Polynuclear Aromatic Hydrocarbon

1.5 Analyte List for the EPH Method

As described in Section 1.1, the EPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons entitled "Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter (MAPEP Interim Final, August, 1994) and the "Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology" (MADEP January, 2003). It is intended to produce data in a format suitable for evaluation by that approach, and that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

The MCP Analyte List for the EPH Method is presented in Table IV B-4. The list is comprised of 17 PAH Analytes, four (4) of which are required for the evaluation of diesel fuel releases, and three (3) collectively quantified extractable hydrocarbon ranges, as identified in Appendix 3 of the EPH Method, that are readily-analyzable using (1) the extraction methods described in Table IV B-2, (2) the cleanup and fractionation procedure described in Section 9.2 (MADEP-EPH-04-1.1), and (3) conventional GC/FID separation and analysis. All the Target PAH Analytes and hydrocarbon ranges that comprise the MCP Analyte List for the EPH Method have hydrocarbon range (e.g., $C_{11} - C_{22}$ aromatic hydrocarbons) or compound-specific MCP Method 1 Groundwater/Soil Standards as described in 310 CMR 40.0974 and 40.0980, respectively. Use of the EPH Method to identify and quantify the listed Target PAH Analytes is optional at the discretion of the data user.

1.5.1 Additional Reporting Requirements for the EPH Method

While it is not necessary to request and report all the Target PAH Analytes listed in Table IV B-3, it is required to quantify the EPH aliphatic and aromatic hydrocarbon ranges, described in the same table, to obtain "Presumptive Certainty" status. Such limitations must be documented for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials as described in Section 2.3.2 of WSC-CAM-VII A, Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP). It is also permissible to quantify EPH Target PAH Analytes, and aliphatic and/or aromatic range concentrations by GC/MS using a "modified" SW-846 Method 8270C as described in Section 9.10 of the EPH Method

The Reporting Limit (based on the concentration of the lowest calibration standard) for each EPH hydrocarbon range or Target PAH Analyte must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, background, etc.) with the exceptions footnoted in Table IV B-4. Meeting "MCP program" reporting limits may require analytical modifications, such as increased sampling weight or volume, to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.

Range/Optional Target Analyte	CASN	MCP Method 1	
		GW-1 (GW-2) µg/L (ppb)	S-1/GW-1 (S-1/GW-3) µg/g (ppm)
Extractable Petroleum Hydrocarbon Ranges:			
C_9-C_{18} Aliphatic Hydrocarbons	NA	(1000)	1000
C_{19}-C_{36} Aliphatic Hydrocarbons	NA	5000	2500
C_{11}-C_{22} Aromatic Hydrocarbons	NA	200	200
Diesel PAH Analytes:			
Naphthalene	91-20-3	20	4
2-Methylnaphthalene	91-57-6	10	4
Phenanthrene	85-01-8	50 [1]	(100)
Acenaphthene	83-32-9	20	20
Other Target PAH Analytes:			
Fluorene	86-73-7	300	400
Acenaphthylene	208-96-8	300	100
Anthracene	120-12-7	2000	1000
Fluoranthene	206-44-0	200 [1]	1000
Pyrene	129-00-0	200	700
Benzo(a)Anthracene	56-55-3	1 [2]	0.7
Chrysene	218-01-9	2 [2]	7
Benzo(b)Fluoranthene	205-99-2	1 [2]	0.7
Benzo(k)Fluoranthene	207-08-9	1 [2]	7
Benzo(a)Pyrene	50-32-8	0.2 [2]	0.7
Indeno(123 cd)Pyrene	193-39-5	0.5 [2]	0.7
Dibenzo(ah)Anthracene	53-70-3	0.5 [2]	0.7
Benzo(ghi)Perylene	191-24-2	300	1000

1. Refers to MCP Method 1 – GW-3 Standard

2. Standard Reporting Limits for this compound may not be able to achieve regulatory compliance limit for water when using the EPH Method for quantification. A GC/MS – SIM, HPLC or some other more sensitive analytical procedure may be required to comply with regulatory requirements for these PAH compounds.

2.0 DATA USABILITY ASSESSMENT FOR THE EPH METHOD

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for the EPH Method, which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

2.1 Specific Guidance Regarding the Interpretation and Use of EPH Data

The EPH Method produces both analyte-specific (Target PAH Analytes) and method defined (hydrocarbon fractions) data. An analyte-specific approach produces data by comparing the response of a known analyte with an unknown concentration to the response of a standard for the same analyte with a known concentration under the same analytical conditions. A method-defined approach produces data by prescriptively defining both analytical conditions and assumptions used to calibrate and interpret the data produced. Such an approach is particularly useful in determining average characteristics for a limited set of analytes with similar physical, chemical and toxicological properties (i.e., the collective concentration of a limited range of hydrocarbons). However, a clear understanding of the analytical limitations of the method and assumptions used to interpret data are required to maximize the potential of using this approach.

Both EPH Target PAH Analytes and ranges are subject to potential "false positive" bias associated with non-specific gas chromatographic analysis. That is (1) other compounds co-eluting at the specified retention time may be incorrectly identified and/or quantified (false positive) as a Diesel or Target PAH Analyte; (2) compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions as defined by this method in Sections 3.4, 3.5 and 3.6of the EPH Method, respectively, that elute within the method-defined retention time window would be included in the Peak Area Count (PAC) and result in an overestimation of a fraction's concentration; (3) as described in Section 9.2.3.3 of the EPH Method, the lighter aromatic compounds may be stripped or may break through the silica gel cartridge/column because of mass overloading or excessive eluting solvent volume, resulting in an underestimation of the C_{11} through C_{22} aromatic fraction's concentration; or, (4) also as described in Section 9.2.3.3, insufficient eluting solvent volume may allow aliphatic hydrocarbons to be retained on the silica gel cartridge/column resulting in low recoveries of these fractions.

Confirmatory analysis by a GC/MS procedure or other suitable method is recommended in cases where a Target or Diesel PAH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a hydrocarbon compound not meeting the regulatory definition of a specific hydrocarbon fraction is suspected. ***Dual-column confirmation is suitable for confirmation of optional Target PAH Analytes only.***

The following definitions are provided to assist in the interpretation and evaluation of Extractable Petroleum Hydrocarbon data:

Aliphatic Hydrocarbon: Any organic compound comprised solely of carbon and hydrogen characterized by a straight, branched or cyclic chain of carbon atoms. This class of organic compounds includes alkanes, alkenes, alkynes, cycloalkanes or cycloalkenes.

Aromatic Hydrocarbon: Any cyclic and conjugated organic compound comprised solely of carbon and hydrogen. Aromatic compounds of environmental significance are benzoids that contain benzene or fused benzene rings.

Extractable Petroleum Hydrocarbon: Any hydrocarbon that elutes within the C_9 through C_{18} and C_{19} through C_{36} aliphatic, or the C_{11} through C_{22} aromatic ranges defined by the method. The definition of Extractable Petroleum Hydrocarbon specifically **excludes** all substituted aliphatic or aromatic hydrocarbon derivatives (non-hydrocarbons as defined by the EPH Method), the individual EPH Method Target and Diesel PAH Analytes, surrogates, and/or internal standards that co-elute within these method-specific ranges. The EPH Method is suitable for the separation and quantification of the aliphatic and non-target aromatic components of kerosene, fuel oil #s 2, 4 and 6, diesel fuel, jet fuel (JP-4, 5 and 8) and certain hydrocarbon-based, low to medium viscosity lubricating oils contained within the aforementioned method-defined ranges (C_9 through C_{36}). These aliphatic hydrocarbon ranges correspond to a boiling point range between approximately 150°C and 265°C. Consequently, the EPH Method, in and of itself, is not suitable for the evaluation of lower boiling petroleum products (gasoline, mineral spirits, or certain petroleum naphthas) or higher boiling petroleum products (asphalts, tars, etc) outside the dynamic range of this method.

Total Petroleum Hydrocarbons (TPH): The collective concentration associated with the PAC for all peaks corresponding to any fractionated or unfractionated aliphatic and/or aromatic compounds eluting between 0.1 minutes before the retention time for n-C_9 to 0.1 minutes after the Rt for n-C_{36}, **excluding** the PAC for all substituted aliphatic or aromatic hydrocarbon derivatives, the individual EPH Method Target and Diesel PAH Analytes, surrogates, and/or internal standards that co-elute within this chromatographic range. The Department recommends that the analysis of the unfractionated EPH extract be used as a conservative estimate of TPH, as this term is defined in 310 CMR 40.0006, when this parameter is used to support human health risk characterization or other MCP assessments and evaluation decisions.

2.1.1 Interfering Peaks in Specified Aliphatic Hydrocarbon Ranges

Hydrocarbons (and non-hydrocarbons), even with elution times within the defined chromatographic windows for the aliphatic hydrocarbon ranges specified by the EPH Method, need not be included in the PAC for these ranges unless they meet the definitions of aliphatic hydrocarbon and extractable petroleum hydrocarbon, as defined above. If the concentration of a hydrocarbon range is based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern is not apparent, the laboratory should provide this information and alert the data user of the potential for a false positive result in the Environmental Laboratory case narrative. MCP sites with co-mingled

non-petroleum hydrocarbons such as vegetable oils, synthetic oils and lubricants, and some naturally occurring humic materials are particularly susceptible to this type of interference.

2.1.2 Interfering Peaks in Specified Aromatic Hydrocarbon Range

The EPH Method should be used with caution at sites with uncertain history and disposal practices, particularly at sites where other hazardous materials were used, stored and/or managed. Such contaminants, if encountered, may co-elute within the method-defined aliphatic and or aromatic ranges resulting in an overestimation of the concentration (i.e., positive interference).

2.1.3 Evaluation of Individual Hydrocarbons Not Associated with an Extractable Petroleum Hydrocarbon

In general, it may be prudent to confirm all FID data using SW-846 Method 8270C (GC/MS) if critical MCP decision-making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the EPH Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with EPH in either aliphatic or the aromatic fraction or with a Target or Diesel PAH Analyte, and such interference would adversely effect MCP decision-making, if confirmed, then SW-846 Method 8270C, Semi-Volatile Organics by GC/MS, should be employed to accurately identify and quantify the components that comprise a fraction or to resolve any uncertainty regarding the identification of a specific Target or Diesel PAH Analyte.

It is recommended that the chromatographic conditions specified under SW-846 Method 8270C be modified for consistency with the conditions specified by the EPH Method to better allow for a direct comparison of the suspect FID peaks with the GC/MS system. This is particularly useful when comparing “suspect” aliphatic hydrocarbons. The electron impact mass spectra for aliphatic hydrocarbon homologues are not particularly unique and chromatographic relative retention time data may also be required to confirm suspect EPH data.

2.1.5 Ineffective Separation of Aromatic and Aliphatic Fractions During Silica Gel Cleanup and Fractionation Step

The amount of hexane used to elute the aliphatic component of the EPH hydrocarbon mixture is critical. An excessive volume of hexane may cause the lighter aromatics to breakthrough and be captured in the aliphatic fraction; while an insufficient volume of hexane may allow some of the heavier aliphatic hydrocarbons to be retained on the silica gel cartridge/column resulting in a lower recovery for these aliphatic fractions. Depending on the analytical conditions, this could result in an underestimation of the C_{11} through C_{22} aromatic fraction’s concentration for the excessive hexane condition or an overestimation of the aromatic fraction for the deficient hexane condition. It should be noted that acceptable recovery of the Fractionation Surrogate Standards, described in Section 7.5 of the EPH Method, may not always provide absolute confirmation that effective separation of the aliphatic fraction from the aromatic fraction of the sample extract has been accomplished.

If ineffective fraction separation is suspected, even with acceptable recovery of the Fractionation Surrogate Standards, SW-846 Method 8270C, Semi-Volatile Organics by GC/MS, may be employed

to accurately identify and quantify the components that comprise a suspect fraction to resolve the uncertainty. Alternatively, if aromatic breakthrough is suspected, the aliphatic fraction may be analyzed to determine if naphthalene or any of the other more "mobile" aromatics are present. See Section 10.4.2 of the EPH Method.

If ineffective fraction separation is confirmed, the elution volume for optimal fractionation efficiency for the specific silica gel lot should be re-established as described in Section 10.4.3.7 of the EPH Method. ***For particularly difficult separations, it may be required to resort to multiple cartridge or column cleanup/fractionation.***

2.2 Substitution of GC/MS for the Identification and Quantification of Ranges and Target Analytes

Consistent with Section 11.3.1.1 (Note 1) of the EPH Method, use of a GC/MS detector operated in the Total Ion Current mode to quantify the EPH Method's aliphatic and aromatic hydrocarbon ranges is not considered a "significant modification" provided that (1) the sample extract has been **fractionated**; (2) the GC/MS system was also used to identify and quantify the Target PAH Analytes in the sample's aromatic fraction; and (3) the QC requirements and performance standards specified in Section 9.10 of the EPH Method are satisfied.

The EPH Method allows for "significant modifications", such as the use of a GC/MS detector to identify and quantify the EPH aliphatic and aromatic hydrocarbon ranges of an **un-fractionated** sample extract, provided that adequate documentation exists, or has been developed to demonstrate an equivalent or superior level of performance. Be advised, however, that any adaptation to the EPH Method that constitutes a "significant modification" pursuant to Section 11.3.1.1 will preclude obtaining "Presumptive Certainty" status for any analytical data produced using such modification and must be disclosed and documented on an attachment to the EPH Method analytical report form, as described in Section 11.3 and Appendix 3 of the EPH Method.

Any major modification to the EPH Method is deemed to satisfy the requirement "to demonstrate an equivalent or superior level of performance" for the determination of the collective concentrations of specified EPH aliphatic and aromatic ranges in water and soil/sediment matrices when:

1. The analytical data produced by the candidate method modification is in a format that is suitable for the evaluation using the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994 and Updated Draft, 2003);

2. The analytical data produced by the candidate method modification for both the EPH aliphatic and aromatic ranges and Target PAH Analytes must have the requisite accuracy and precision to be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000) consistent with the analytical data quality requirements of 310 CMR 40.0017;

3. The reported concentration for the C_9 –C_{18} Aliphatic Hydrocarbon range includes the preponderance of the individual C_9 through C_{18} aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment;

4. The reported concentration for the C_{19} –C_{36} Aliphatic Hydrocarbon range includes the preponderance of the individual C_{19} through C_{36} aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment; and

5. The reported concentration for the C_{11} –C_{22} Aromatic Hydrocarbon range includes the preponderance of individual C_{11} through C_{22} aromatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment.

3.0 REPORTING REQUIREMENTS FOR THE EPH METHOD

Analytical reporting requirements for the EPH Method are presented in Table IV B-3 and are summarized below in Table IV B-5 as "Required Analytical Deliverables". These reporting requirements must be included as part of every analytical deliverable for the EPH Method. It should be noted that although certain items are not specified as "Required Analytical Deliverables", these data must be available for review during an audit. The required information and format for data reporting for EPH and TPH are presented in Appendix 3 of the EPH Method.

3.1 General Reporting Requirements for the EPH Method

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory case narrative contents in WSC-CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for the EPH Method

Specific Quality Control Requirements and Performance Standards for the EPH Method are presented in Table IV B-3. Specific reporting requirements for the EPH Method are summarized below in Table IV B-5 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.

Table IV B-5 Analytical Reporting Requirements for the EPH Method

Parameter	Method Section Reference	Required Analytical Deliverable
GC Performance	10.2 and 10.4	NO
Retention Time Windows	9.6	NO
Initial Calibration	9.7.2	NO
Calibration Check Standard	10.4.3.1	NO
Laboratory Method Blank	10.4.3.2	YES
Laboratory Control Sample (LCS)	10.4.3.3	YES
LCS Duplicate	10.4.3.4	YES
Initial Calibration Verification (ICV)	10.4.3.5	NO (run only if separate source standard is not used for LCS)
Matrix Spike (MS)	10.4.4.2	YES (if requested by data user)
Matrix Spike Duplicate (MSD)	10.4.4.2	YES (if requested by data user)
Matrix Duplicate	10.4.4.1	YES (if requested by data user)
Extraction Surrogates	10.4.1	YES
Fractionation Surrogates	10.4.1	YES
Fractionation Check Standard	10.4.3.7	YES
Aromatic Breakthrough Evaluation	10.4.2	YES
System Solvent Blank (for baseline correction only)	10.4.3.6	YES See the EPH Method, Section 11.2.5
GC/MS QC Parameters	9.10	YES (GC/MS only) See WSC-CAM II B, Table II B-3
General Reporting Issues	11.3	Data Reporting Format is Presented in Section 11.3

3.2.1 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the EPH target PAH analytes or hydrocarbon ranges exceed the concentration of their respective highest calibration standard, or any non-target peak exceeds the dynamic range of the detector (i.e., "off scale"), the Reporting Limit (RL) for each EPH target PAH analyte or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Extract Volume (mL) + Diluent Volume (mL)}}{\text{Sample Extract Volume (mL)}}$$

And the revised RL for the diluted sample extract, RL_d:

RL_d = DF X Lowest Calibration Standard for Target PAH Analyte (or hydrocarbon range)

It should be understood that sample extracts with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample extract dilution that enables quantification of target analytes or ranges, which exceed the calibration range. All dilutions must be fully documented in the Environmental Laboratory case narrative.

Analytical Note: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte in the sample extract must be at least 60 to 80% of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes, which did not require dilution.

If a sample analysis results in a saturated detector response for any target or non-target compound, the analysis must be followed by a System Solvent Blank analysis. If the solvent blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a solvent blank demonstrates the lack of system interferences.

Appendix IV B I

Sample Collection, Preservation, And Handling Procedures for the EPH Analysis

1.0 Sampling

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for EPH samples analyzed in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-CAM-VIIA, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP).

{PRIVATE }Matrix	Container	Preservation	Holding Time*
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; **Cool to 4 ± 2° C**	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediments	4-oz. (120 mL) wide-mouth amber glass jar with Teflon-lined screw cap	**Cool to 4 ± 2° C**	Samples must be extracted within 14 days and extracts analyzed within 40 days of extraction
	4-oz. (120 mL) wide-mouth amber glass jar with Teflon-lined screw cap. Jar should be filled to only 2/3 capacity to avoid breakage if expansion occurs during freezing	Freeze at - 10°C in the field or in the laboratory*.	Samples must be extracted within 14 days of the date thawed and extracts analyzed within 40 days of extraction.
* Samples processed in the laboratory must be preserved at 4 ± 2° C and frozen within 48 hours of the time of collection. Frozen samples may be held for up to one year prior to analysis and must be extracted within 24 hours of thawing.			

2.0 Additional Considerations

A chain of custody form must accompany all sample bottles and must document the date and time of sample collection and preservation method used. The pH of all water samples must be determined by the laboratory prior to sample extraction. Any sample with a pH above 2.0 must be so noted on the laboratory/data report sheet and the pH must be re-adjusted below 2.0 with HCl, as soon as possible. The volume of acid added and the re-adjusted pH should also be recorded as a Comment on the EPH laboratory/data report form, or equivalent. See Appendix 3 of the EPH Method.

APPENDIX IV B-2

FLOW Charts Describing the EPH Method's Analytical Process

Exhibit IV B-1 - EPH Method Aqueous Extraction Process

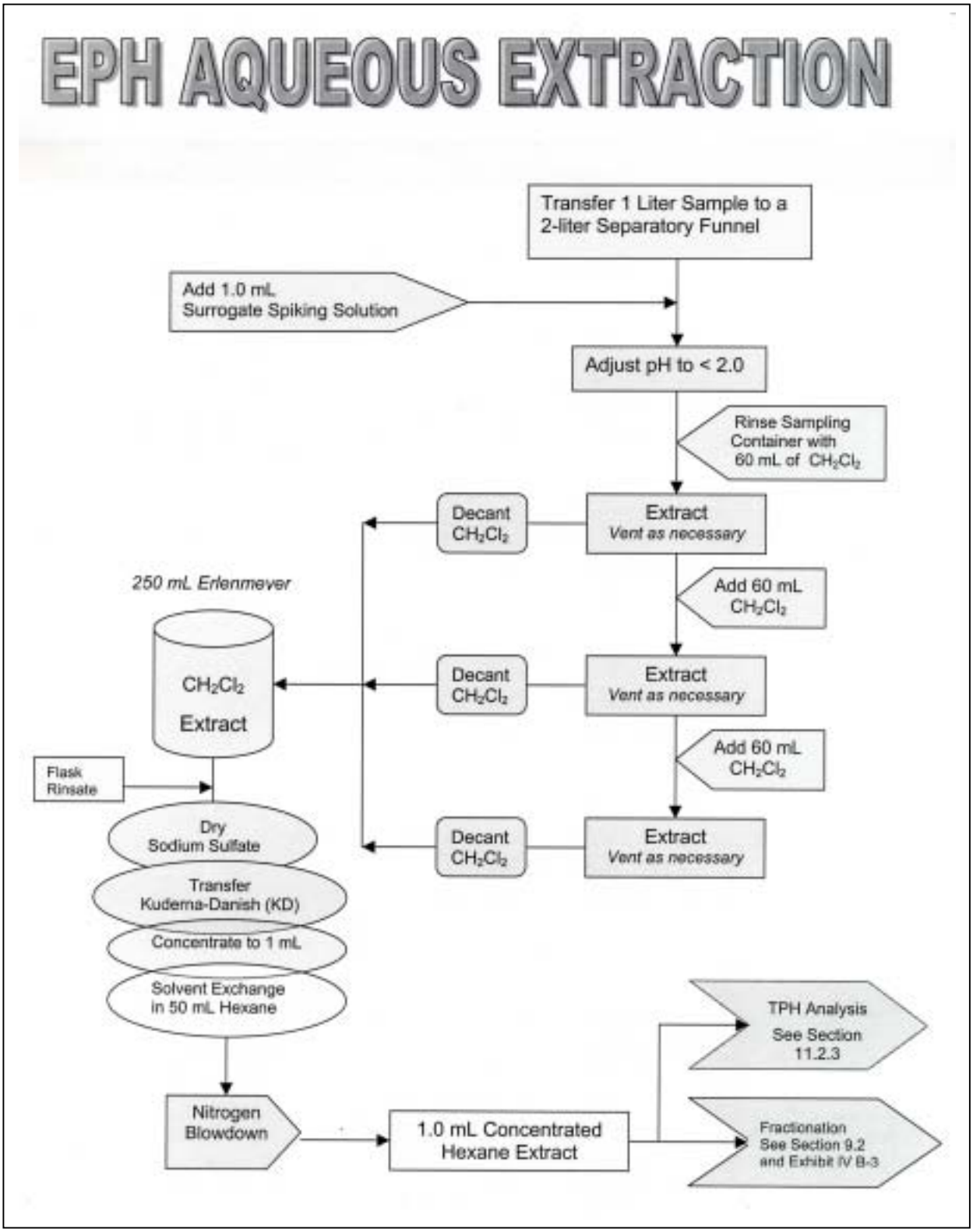

Exhibit IV B-2 - EPH Method Soil/Sediment Extraction Process

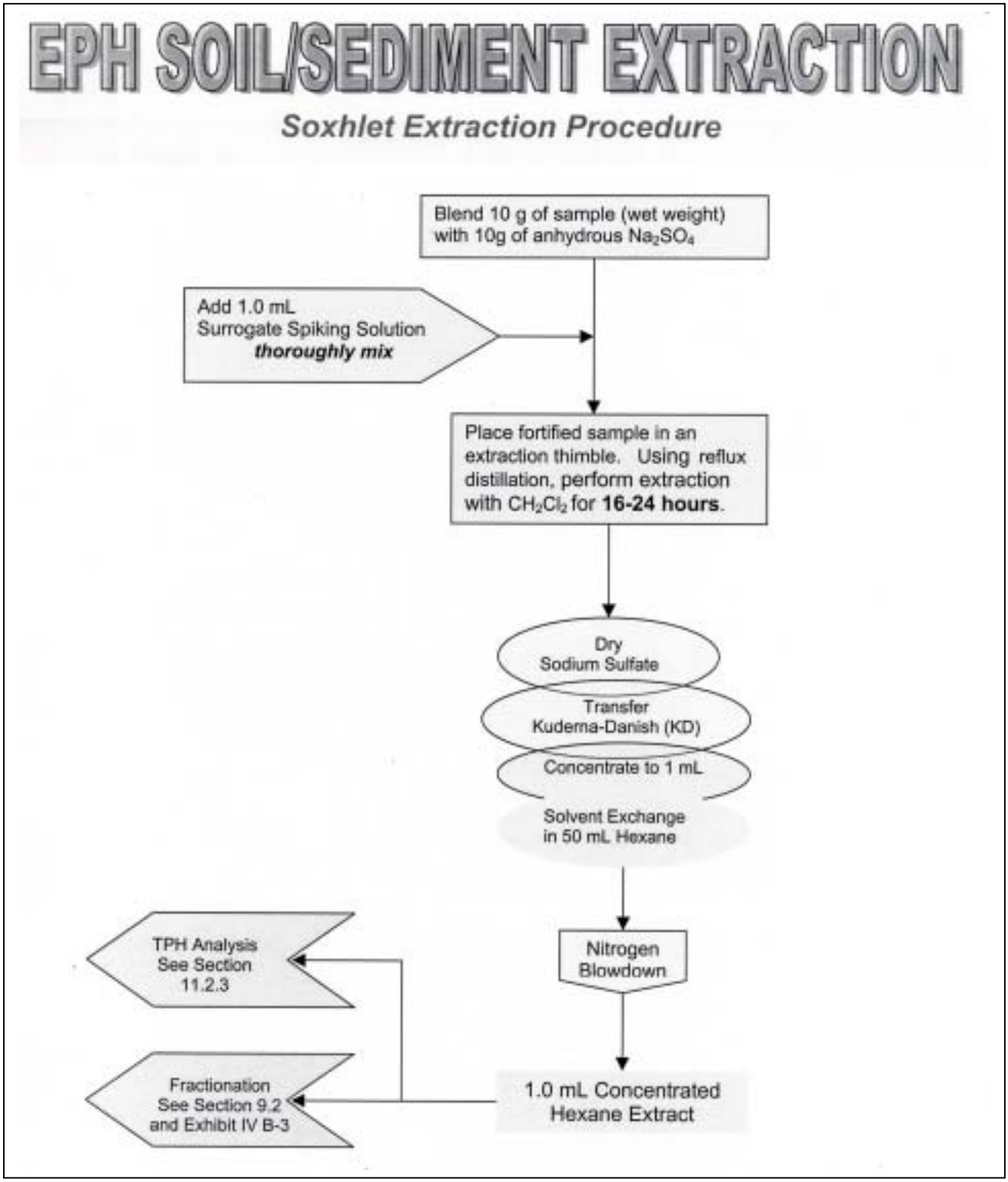

Exhibit IV B-3 - EPH Method Fractionation Process

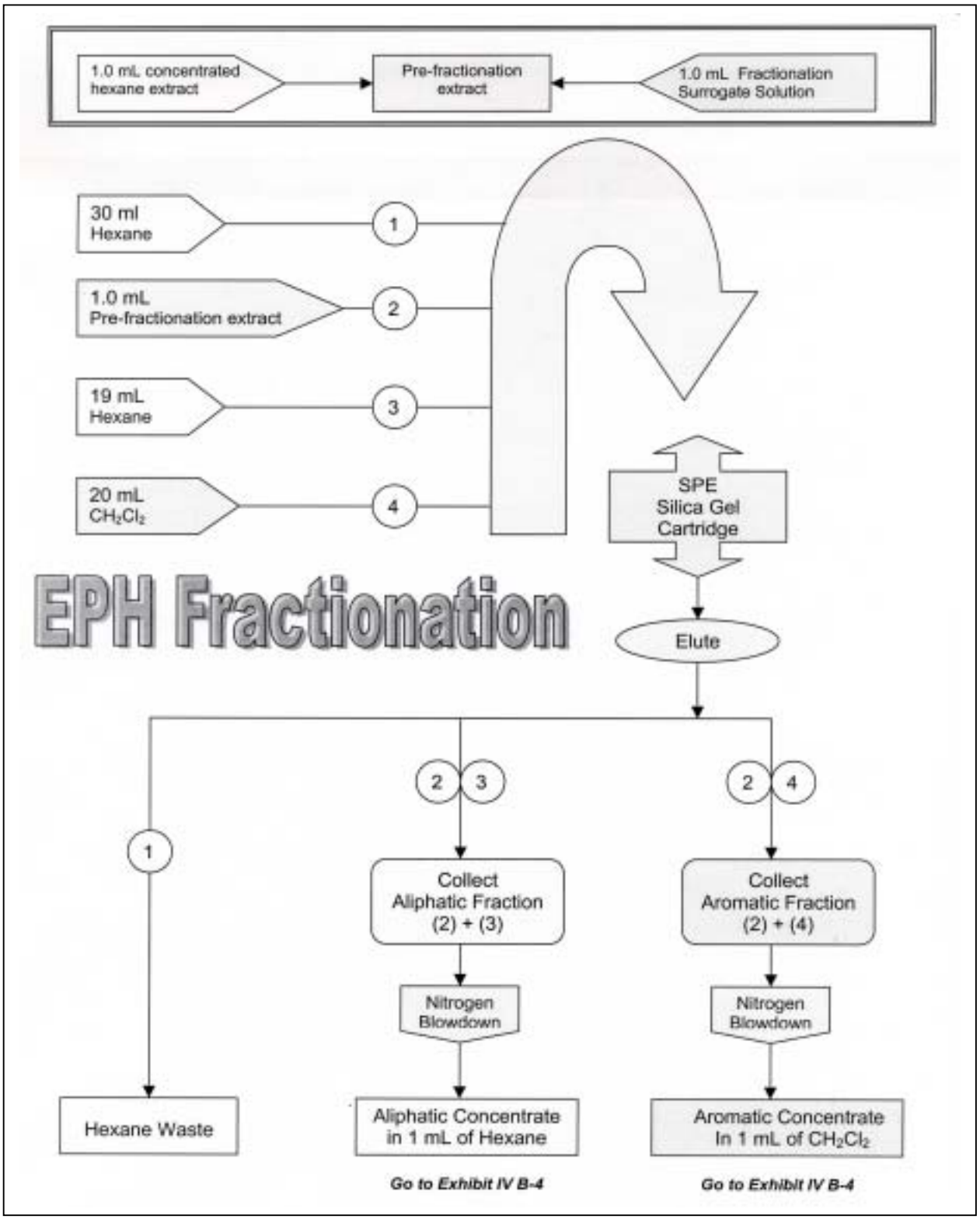

Exhibit IV B-4 - EPH Method Analysis and Quantitation Processes